2018 DOE Vehicle Technologies Office Annual Merit Review

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Lithium Dendrite Prevention for Lithium Batteries

WU XU (PI) and JI-GUANG ZHANG

Pacific Northwest National Laboratory

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project ID #bat275

Overview

Timeline

- Start date: Oct. 2015
- End date: Sept. 2018
- Percent complete: 85%

Barriers

- Growth of lithium dendrites
- Low Coulombic efficiency
- Low charge current density

Budget

- Project funding
  - DOE share 100%
- Funding received in FY17: $340k
- Funding received in FY18: $400k

Partners

- Argonne National Laboratory
- U.S. Army Research Laboratory

Relevance/Objectives

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- Enable lithium (Li) metal to be an effective anode in rechargeable Li-metal batteries using conventional 4-V Li-ion intercalation cathodes for long cycle life at a reasonably high current density.
- Explore various factors that affect the morphology of Li deposition and suppress Li dendrite formation on Li-metal anode.
- Develop nonaqueous electrolytes and additives to protect Li metal anode and to increase Li Coulombic efficiency (CE).
- Develop hybrid polymeric composite electrolytes to protect Li metal anode.
- Improve the stability and the conductivity of solid electrolyte interphase (SEI) layer on Li metal anode to enable long cycleability.

Milestones

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Date	Milestones	Status
June 2017	Identify new electrolytes that are stable with both Li and high voltage cathode	Completed
Sept. 2017	Further Increase CE of Li cycling in the new electrolyte	Completed
Dec. 2017	Develop a lithium salt mixture that has an ambient melting temperature and an ionic conductivity over 1 mS/cm	Completed
March 2018	Investigate effects of inorganic fillers and polymers on hybrid composite electrolytes	Completed
June 2018	Develop an inorganic/polymeric hybrid composite electrolyte with ionic conductivity over 1 mS/cm and Li CE over 99%	On track
Sept. 2018	Achieve over 300 cycles for 4-V Li||NMC batteries with ~ 2 mAh/cm^2 cathode loading	On track

Approach

- Develop new electrolyte formulations (including salts and additives in carbonate solvent mixtures) to achieve high Li CE and stable with high voltage cathode.
  - Investigate effects of Li capacity utilization and charging current density on stability of Li metal anode.
  - Study effects of four imide-orthoborate dual-salt mixtures on electrolyte stability and protection of Li metal anode.
  - Develop new electrolytes based on LiTFSI-LiBOB/carbonate to enhance Li metal battery performances.

- Develop new hybrid polymeric composite electrolytes to protect Li metal anode and enhance cycling performance of Li metal batteries.
  - Investigate effects of polymer separators on Li metal stability.
  - Develop new hybrid polymeric composite electrolytes.

Technical Accomplishments

Li capacity utilization and charge current density largely affect Li morphology, stability and SEI compositions

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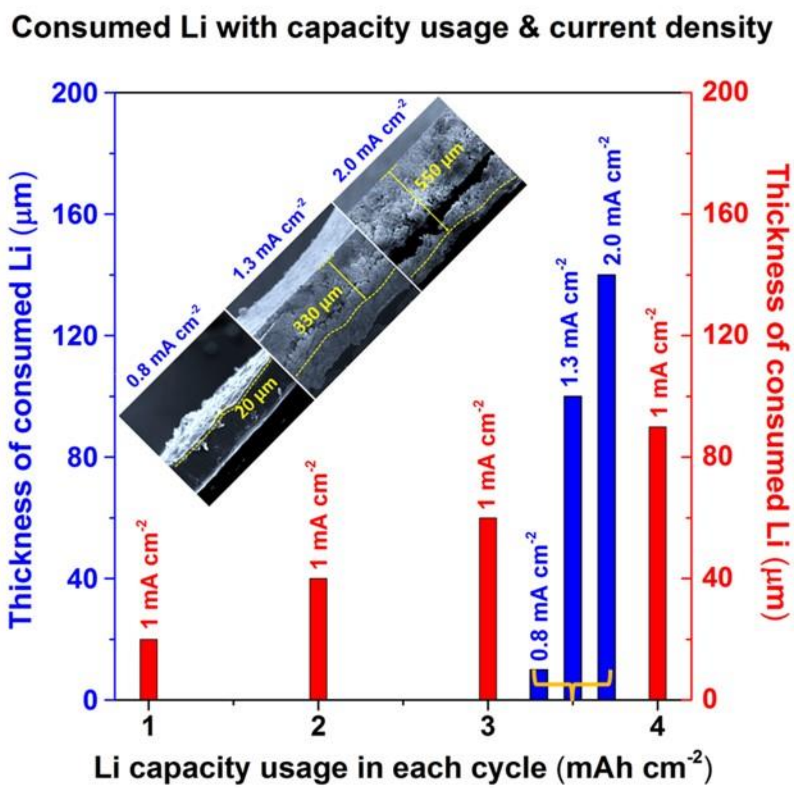
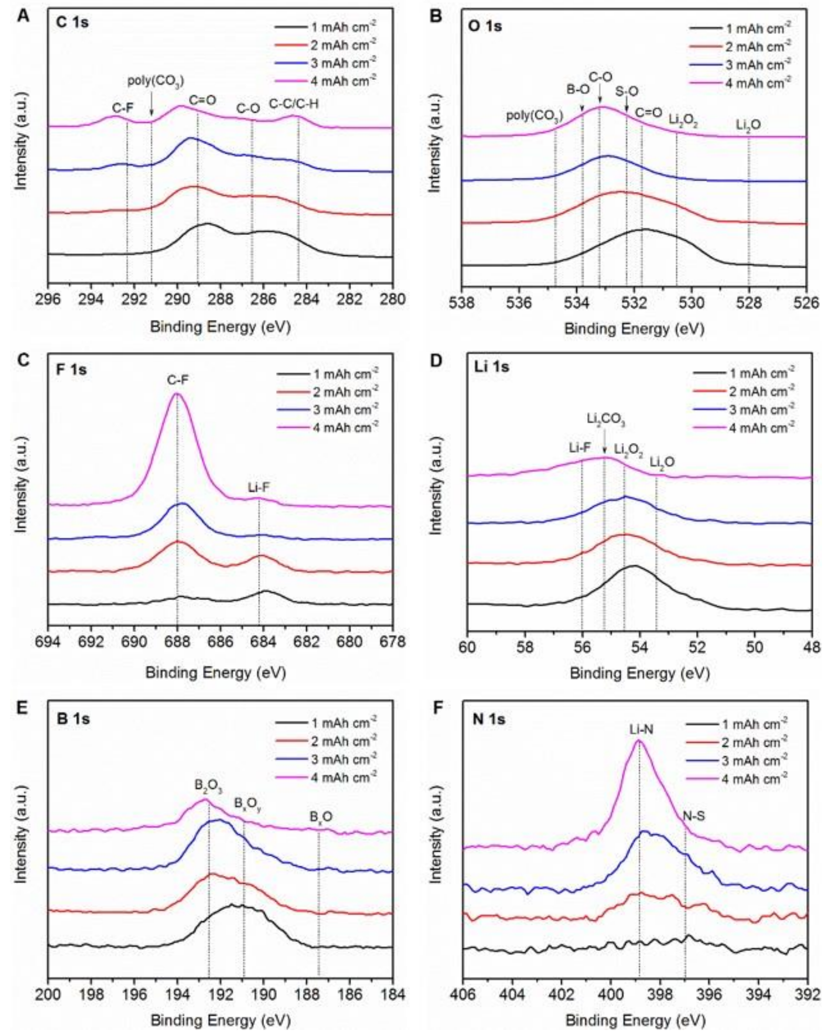
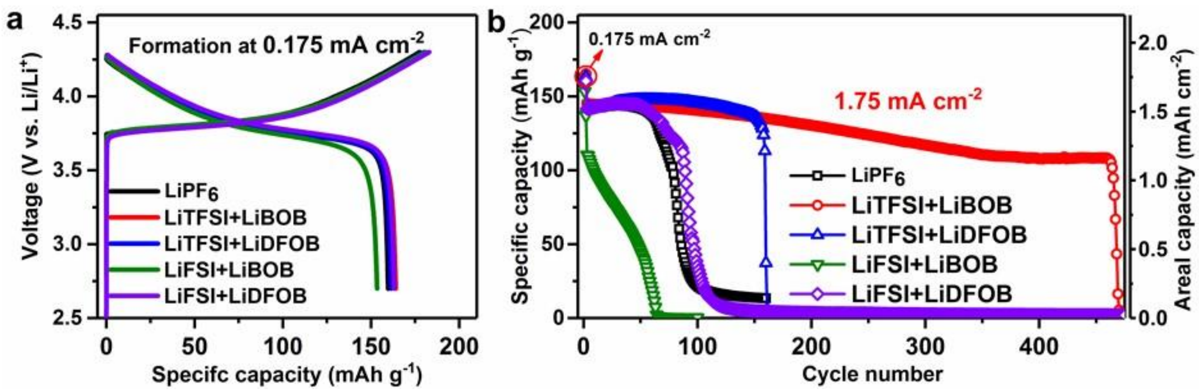




- Li capacity utilization changes SEI compositions on Li anode.
- Slow charge rate leads to a similar Li metal expansion ratio with Li capacity usage.
- Charge current density has more effect on Li stability than Li capacity utilization.

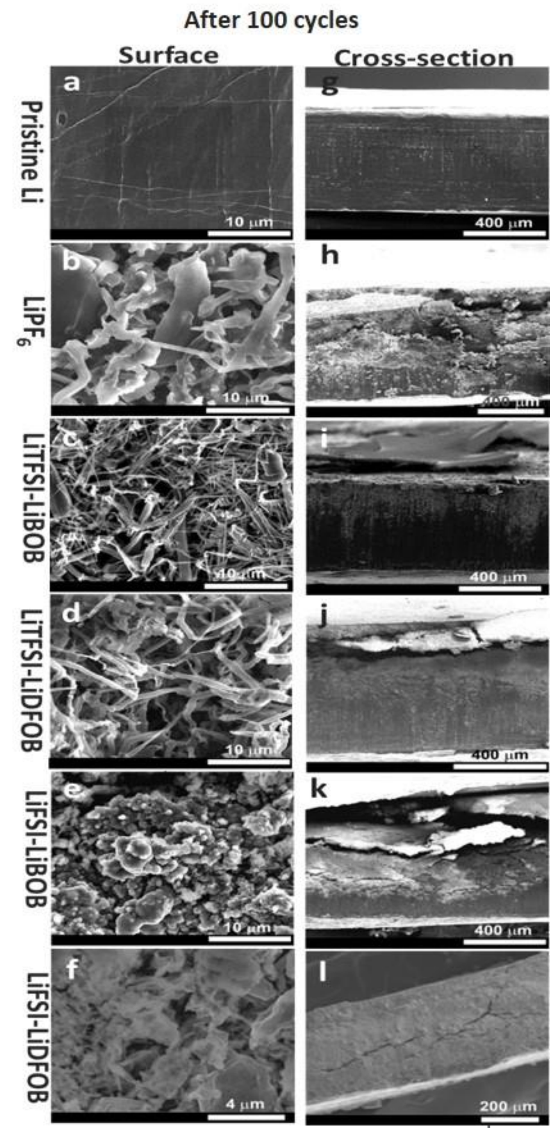
Technical Accomplishments

Imide-orthoborate dual-salts affect cycling performance and morphology of Li metal anode



Types of dual-salts	Disproportionation reaction	Reaction energies (kJ mol^{-1})	
		Electrochemical (two radicals)	Chemical (two anions)
TFSI+BOB	$CF_3SO_2NSO_2CF_3 + (C_2O_4)B(O_4C_2) \rightarrow CF_3SO_2NSO_2OC(=O)C(=O)O + CF_3B(O_4C_2)$	487.7	517.9
TFSI+DFOB	$CF_3SO_2NSO_2CF_3 + (C_2O_4)BF_2 \rightarrow CF_3SO_2NSO_2OC(=O)C(=O)O + CF_3BF_2$	244.6	326.9
FSI+BOB	$FSO_2NSO_2F + (C_2O_4)B(O_4C_2) \rightarrow FSO_2OC(=O)C(=O)O + FSO_2NB(O_4C_2)$	47.6	85.0
FSI+DFOB	$FSO_2NSO_2F + (C_2O_4)BF_2 \rightarrow FSO_2OC(=O)C(=O)O + FSO_2NBF_2$	97.1	204.8

- Among four imide-orthoborate dual-salt mixtures, LiTFSI-LiBOB shows highest reaction energies and best cycling stability due to formation of robust SEI on Li metal.



Technical Accomplishments

XPS of cycled Li metal anodes indicates different SEI components and compositions in four dual-salt electrolytes

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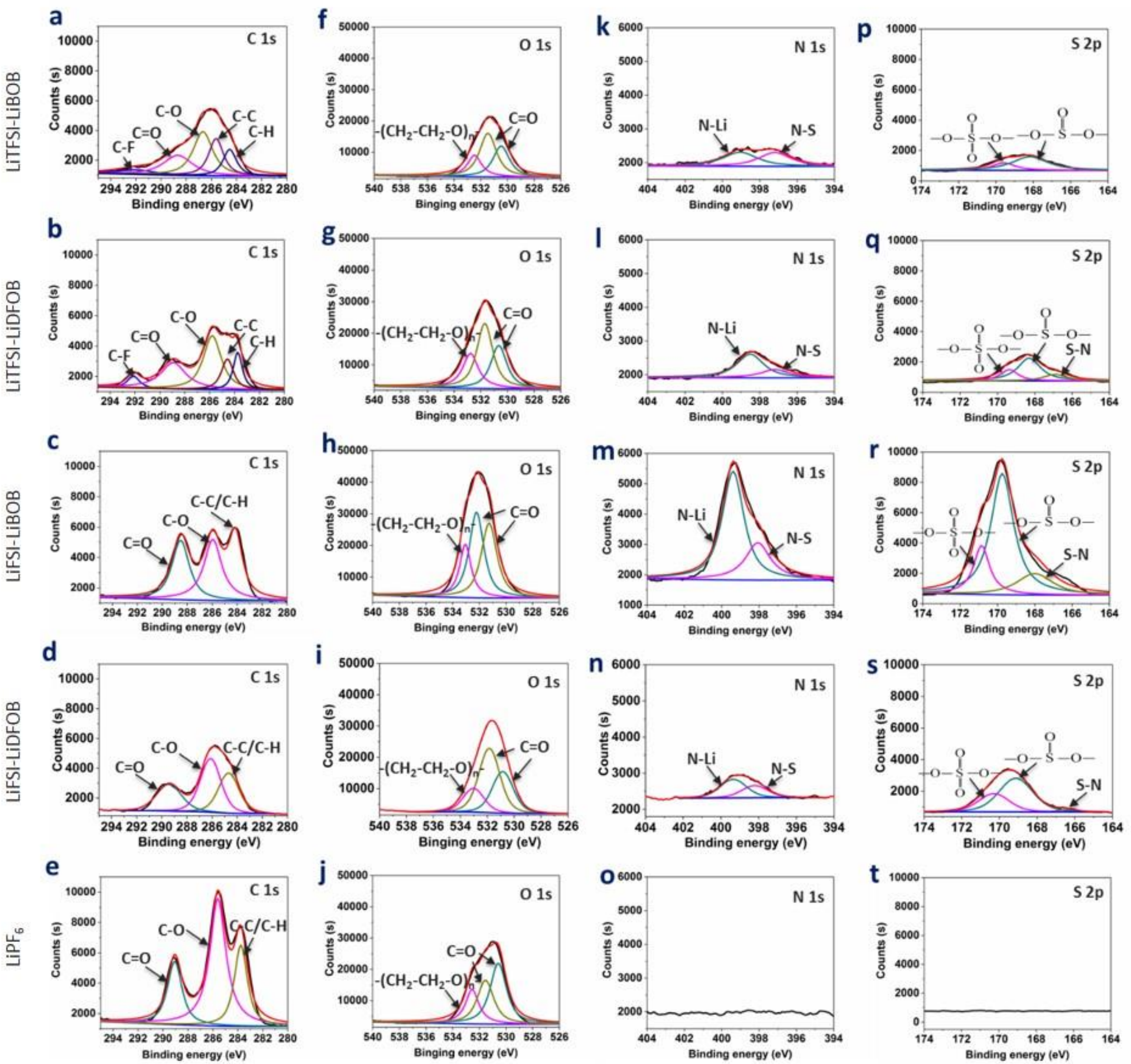

- Different dual-salt electrolytes lead to similar decomposition components on Li surface, but their compositions are different.
- More electrolyte decomposition on Li anode when using LiFSI-LiBOB and LiFSI-LiDFOB electrolytes than that using LiTFSI-LiBOB and LiTFSI-LiDFOB electrolytes.
- LiTFSI-LiBOB electrolyte could result in the least amount of surface film on the Li metal anode among the five studied electrolytes.

Technical Accomplishments

Solvents optimization and additives combination enhance Li protection

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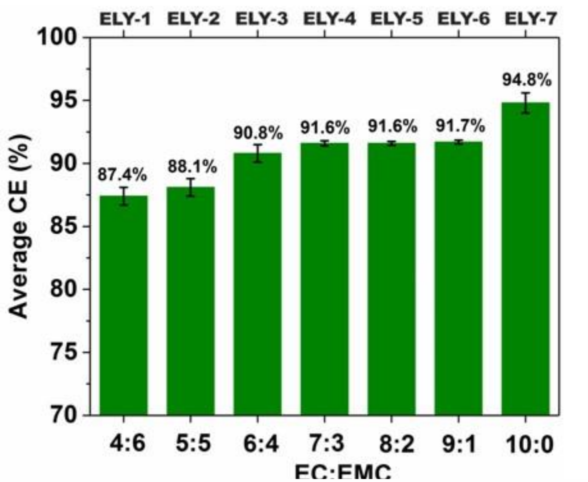
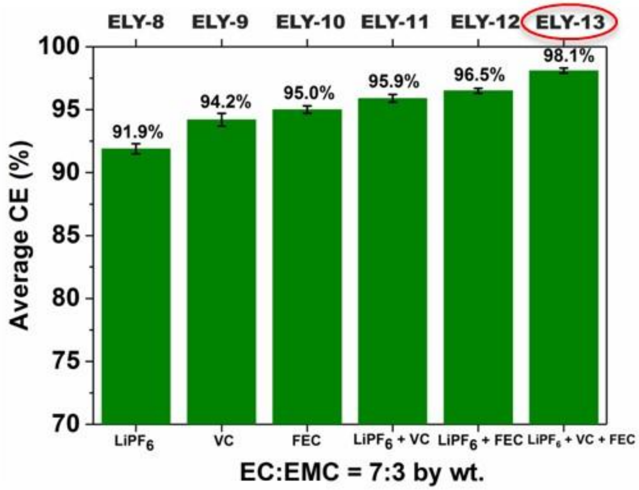
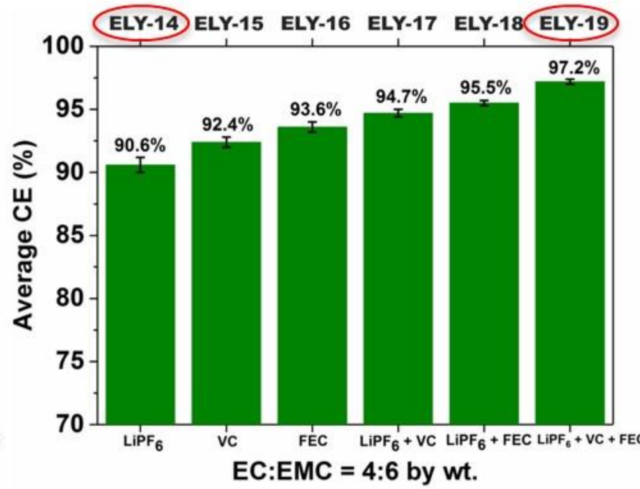
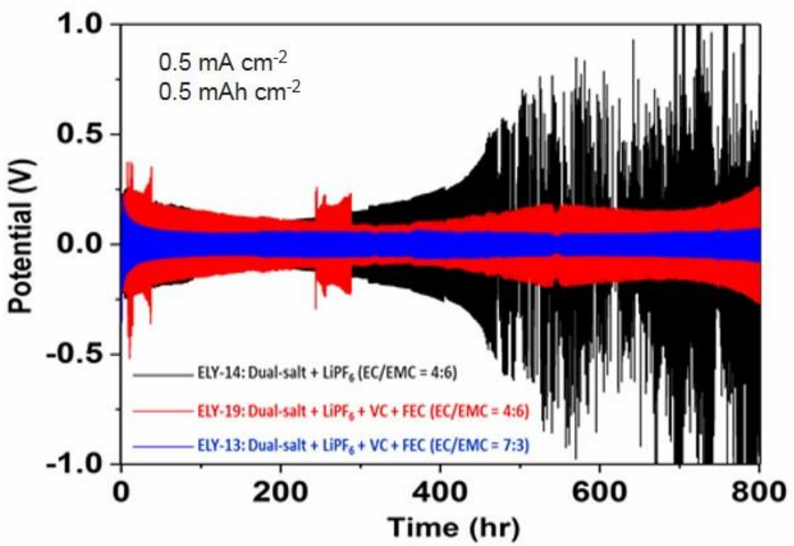




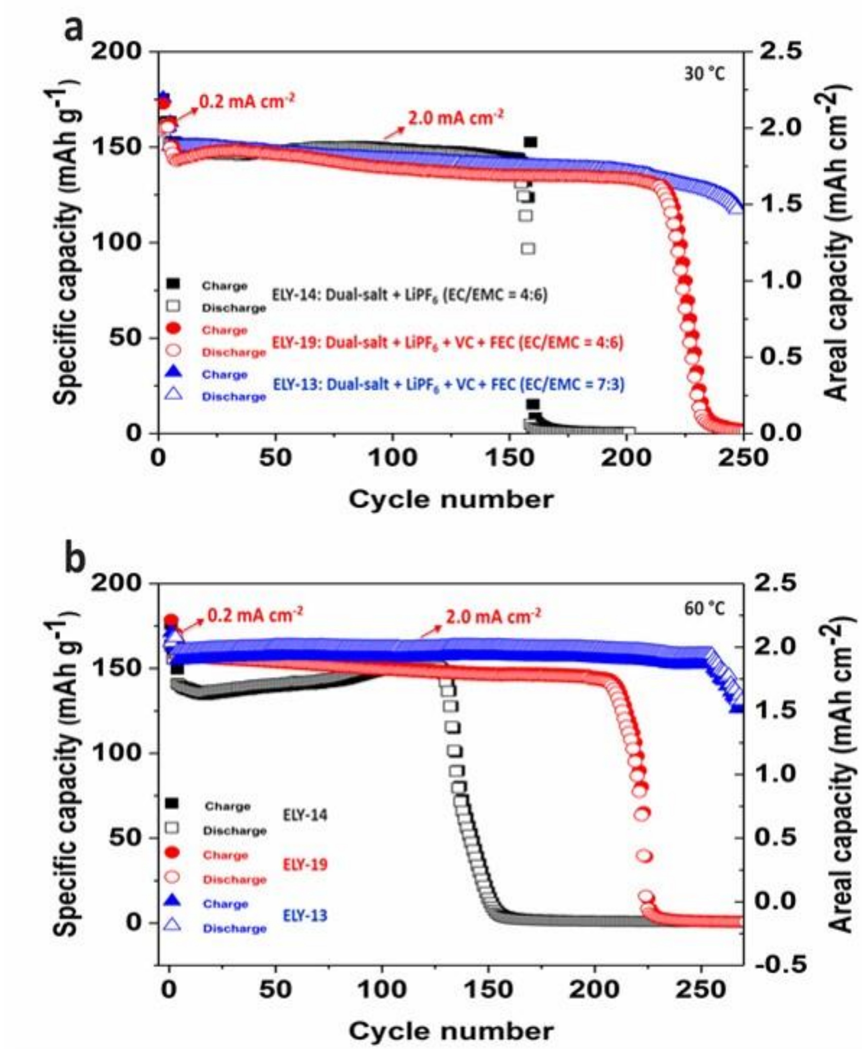


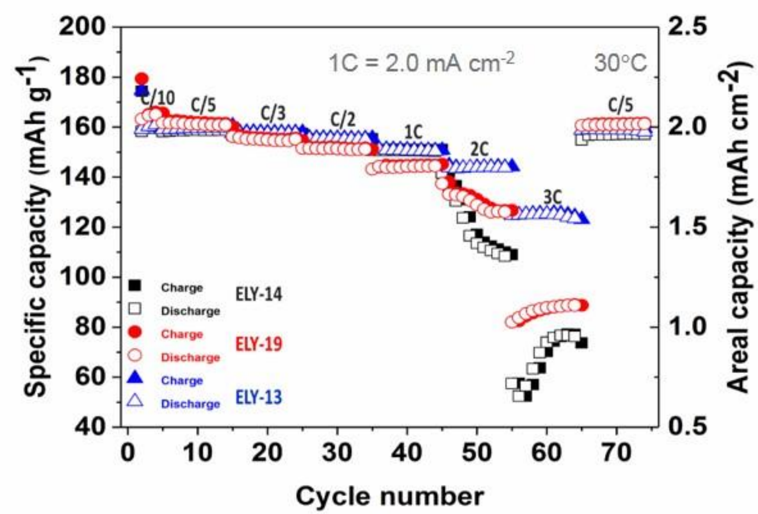


- LiTFSI-LiBOB/EC-EMC as baseline electrolyte.
- Increase EC content in solvent mixture improves average Li CE.
- Combinational additives further improve Li CE.
- The optimal electrolyte (ELY-13), 0.6 M LiTFSI + 0.4 M LiBOB in EC-EMC (7:3 by wt.) with 0.05 M $LiPF_6$, 2 wt% VC and 2 wt% FEC, shows high Li CE of 98.1% and long cycling stability with Li metal anode.

Technical Accomplishments

Optimized electrolyte enhances Li||NMC in long cycling stability and rate capability





- The optimal electrolyte ELY-13 greatly enhances the long-term cycling stability and rate capability of Li||NMC111 cells over the control electrolytes.

Technical Accomplishments

Optimized electrolyte enhances formation of large Li deposits and reduces resistance

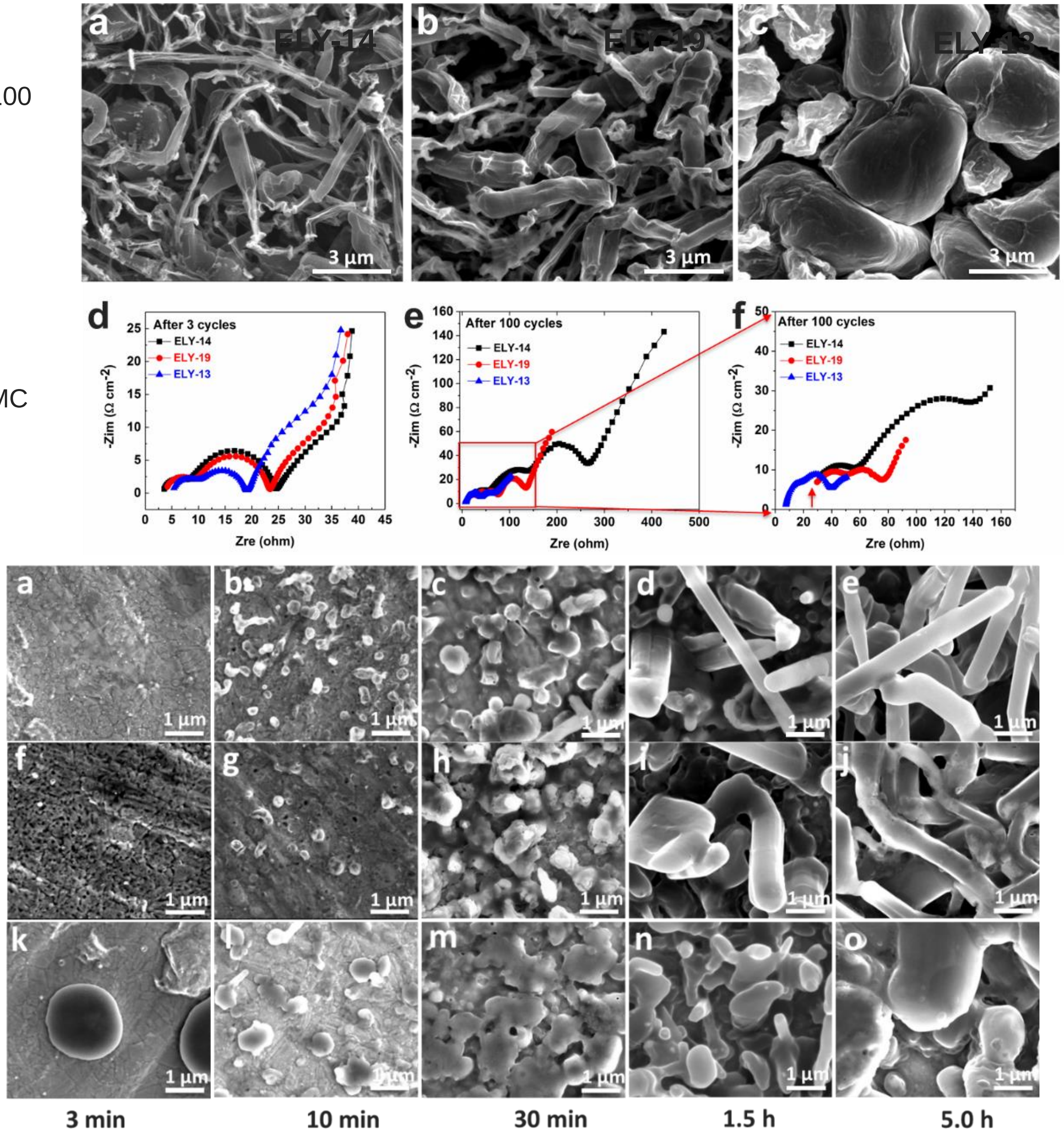
After 100 cycles

Li||NMC cells

ELY-14

ELY-19

ELY-13



- The optimal electrolyte ELY-13 enhances the formation of large size Li deposition, while the controls yield wire-like Li morphology.

- ELY-13 leads to lower surface area of the deposited Li, less side reactions between Li and electrolyte, higher Li CE, lower resistance and longer cycle life of Li||NMC cells.

Technical Accomplishments

Effect of separators on Li CE and Li stability in different electrolytes

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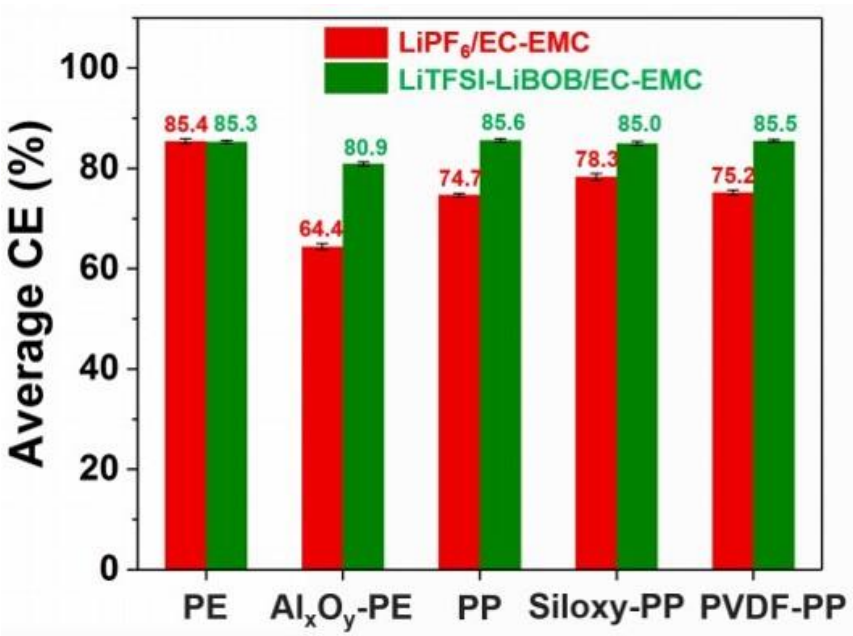
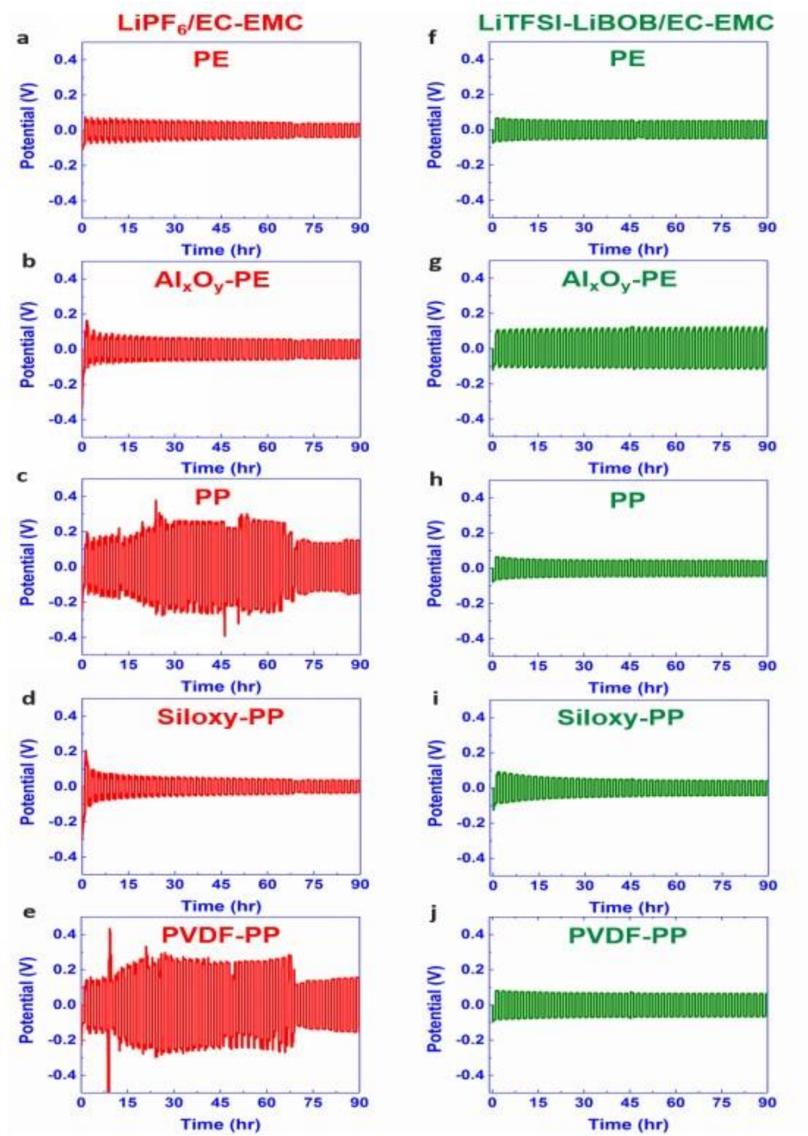
- ❑ Stability of separators (not polymer electrolytes) with Li metal has seldom been studied.
- ❑ Effect of separators on Li CE and Li cycling stability is of great importance for rechargeable Li metal batteries.





- ▶ In $LiPF_6$/EC-EMC electrolyte, separator shows large effect on Li CE and stability of Li||Li cells.
- ▶ In HF-free electrolyte, separator does not affect Li CE but does influence Li polarization.

Technical Accomplishments

Surface morphology of separators change after cycling with Li metal in $LiPF_6$-electrolyte

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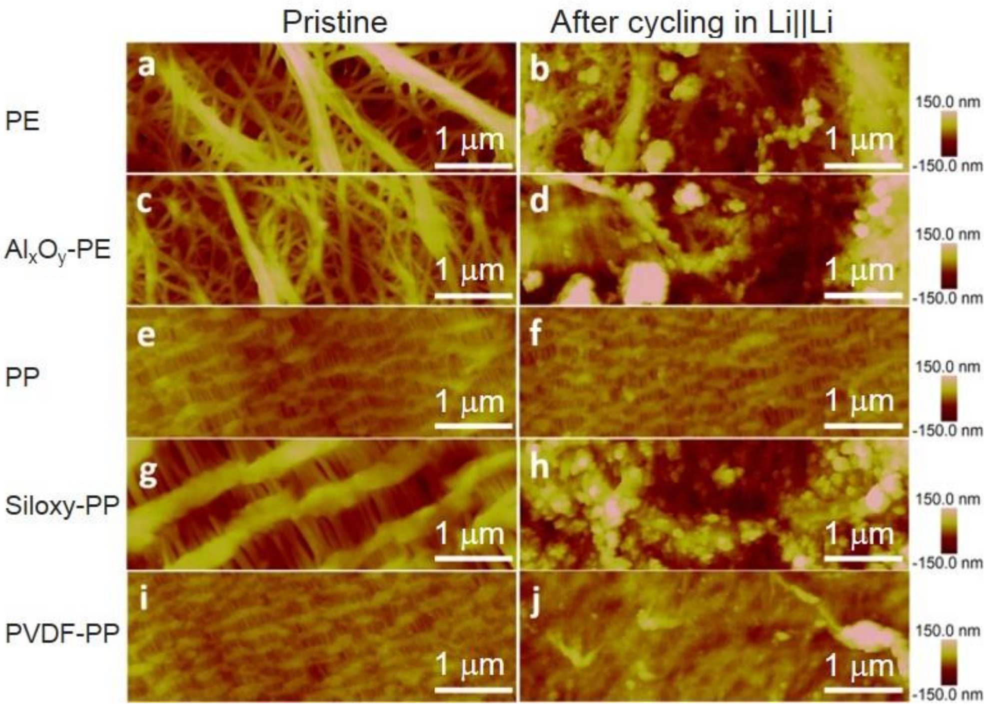
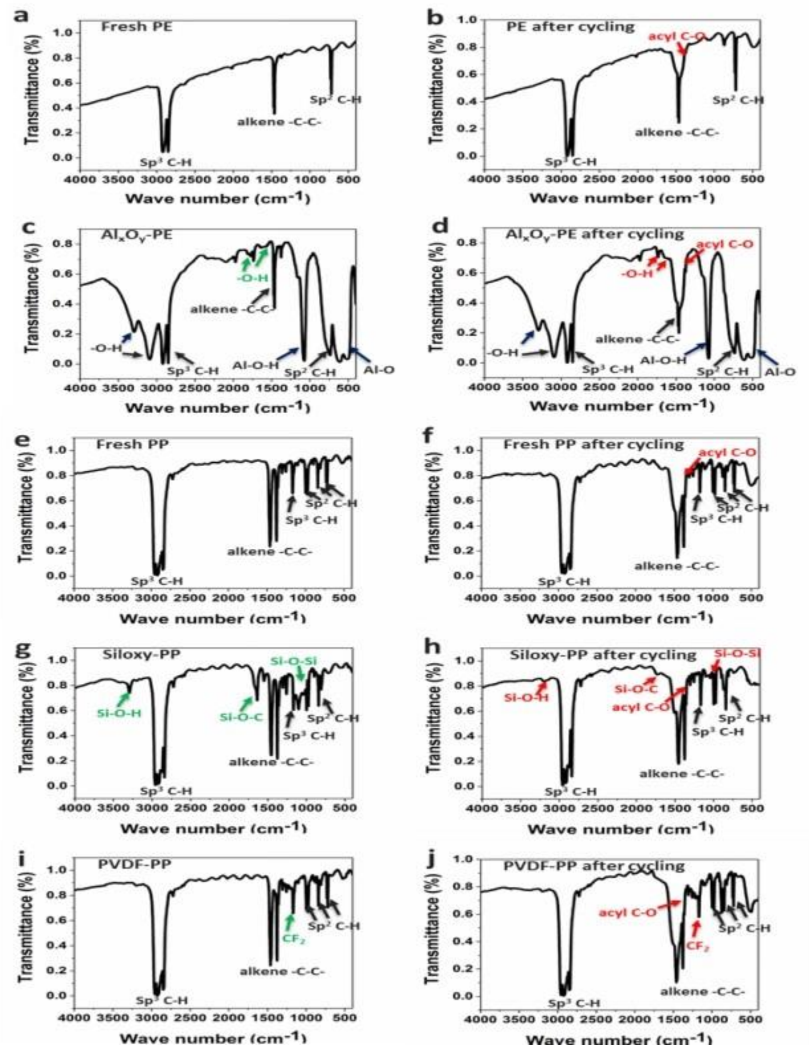


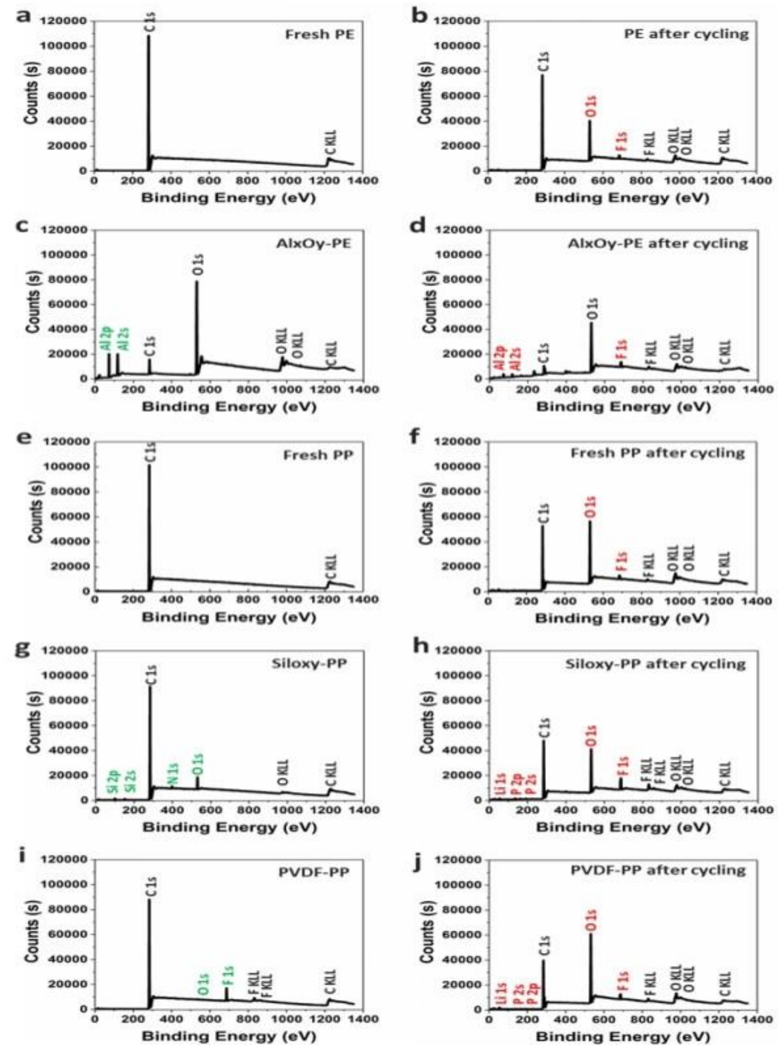
- Cycled separators were retrieved from Li||Li cells with $LiPF_6$/EC-EMC electrolyte after 50 cycles.

- In pristine, the coating layers are not observed.
- After cycling, except for PP, all other four separators show a lot of solid particles or thick films clogged or covered on separators.
- On PE, SEI particles adhesive to separator.
- On Al_xO_y-PE, $Al_xO_y + Li \rightarrow Al + Li_zO$, $Al_xO_y + HF \rightarrow AlF_3 + H_2O$, and $Li + HF \rightarrow LiF + H_2$.
- On Siloxy-PP, forming F-Si-O species.
- On PVDF-PP, forming LiF.
- PP has less adhesion to SEI particles.

Technical Accomplishments

FTIR and XPS results indicate changes of separators after cycling with Li metal in $LiPF_6$-electrolyte for 50 cycles





- Cycled separators are either unstable with Li or adhesive with SEI components.

Technical Accomplishments

Development of mixed salts electrolytes with ionic liquids

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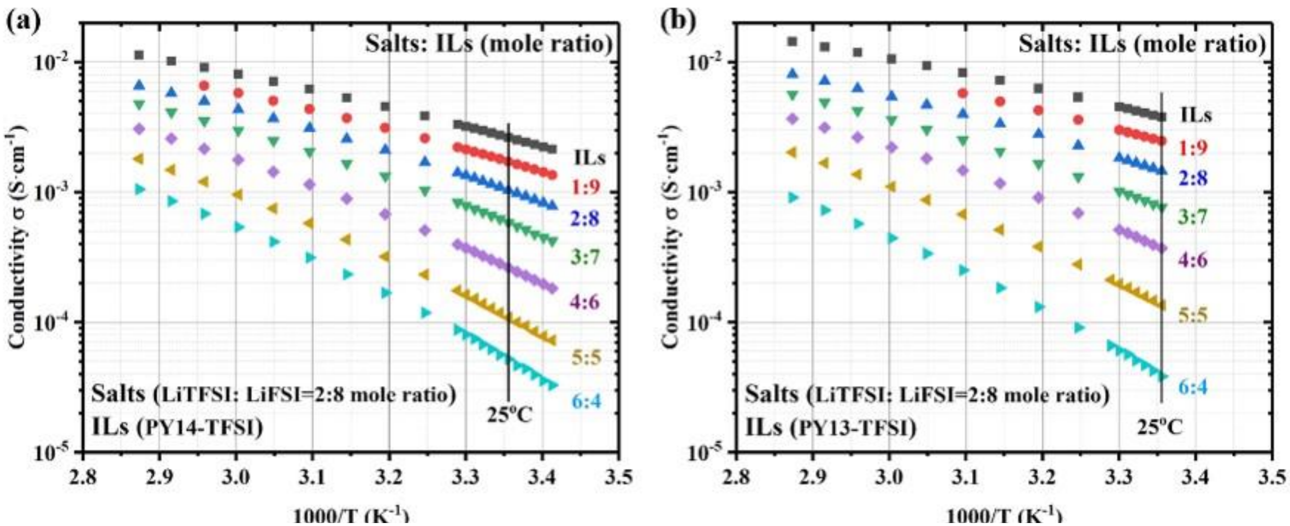
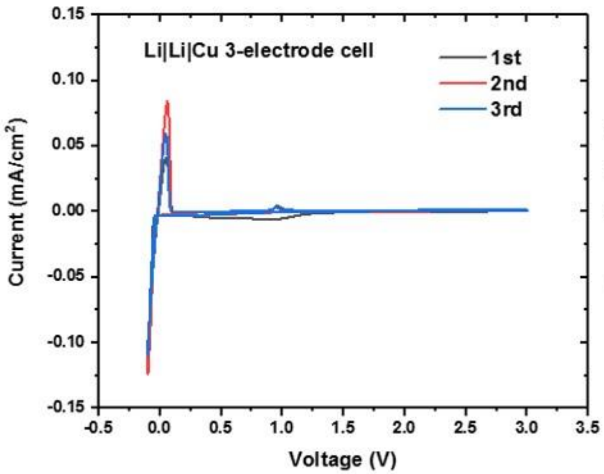
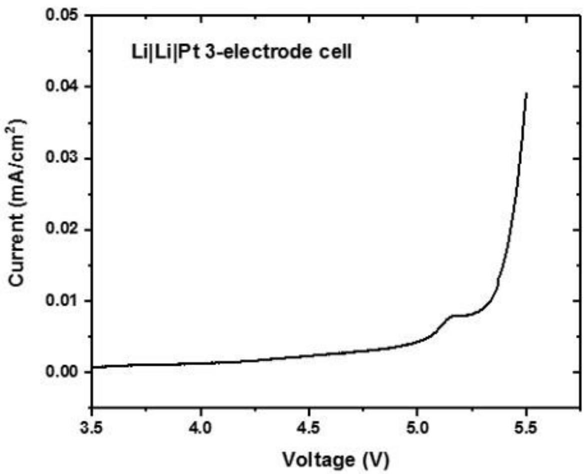
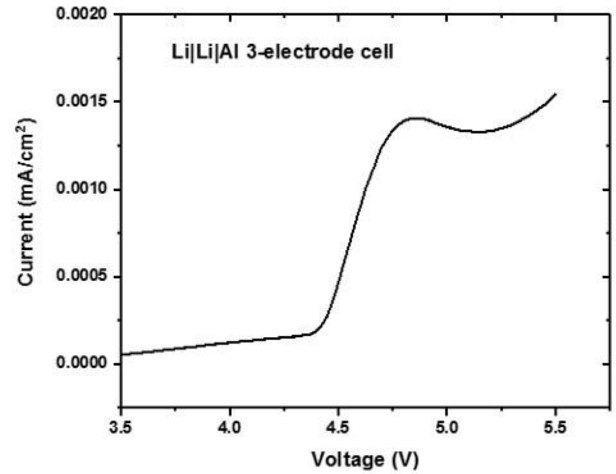


- LiTFSI-LiFSI (2:8 by mol) dual-salt mixtures with certain amount of room temperature molten salts (i.e. ionic liquids) at $(LiTFSI\text{-}LiFSI)_{0.2}\text{-}IL_{0.8}$ show an ionic conductivity of 1.0 ~ 1.4 mS cm^{-1} at 25°C.







- Good electrochemical stability of $(LiTFSI\text{-}LiFSI)_{0.2}\text{-}IL_{0.8}$ on both cathode and anode.

Technical Accomplishments

Electrochemical performance of polymer-in-salt electrolyte

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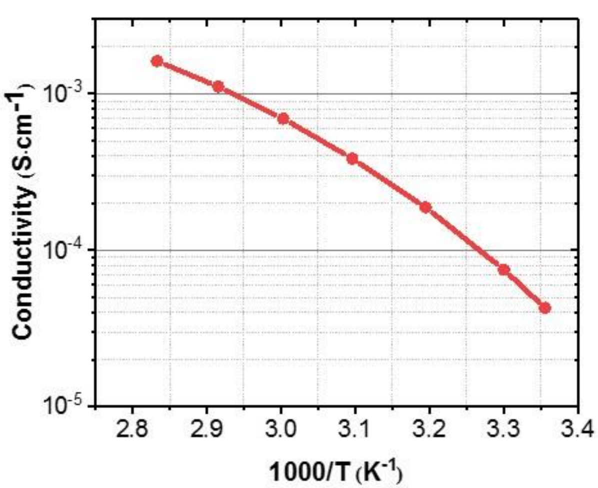

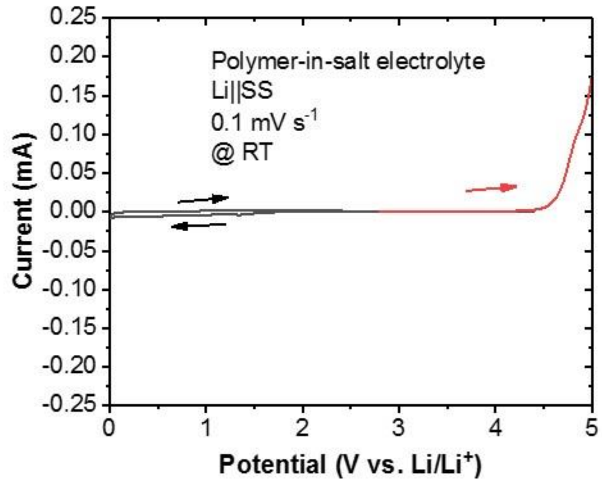

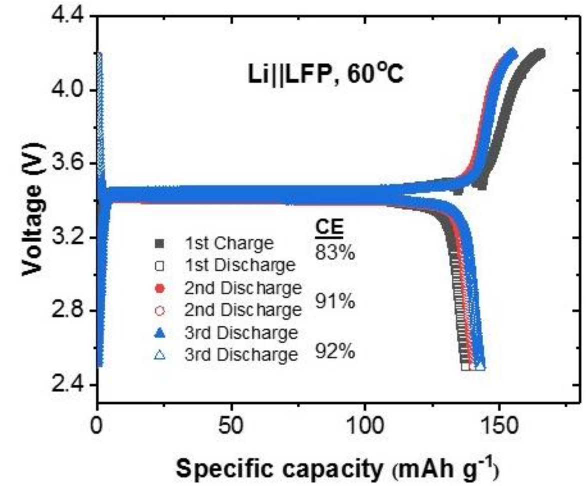

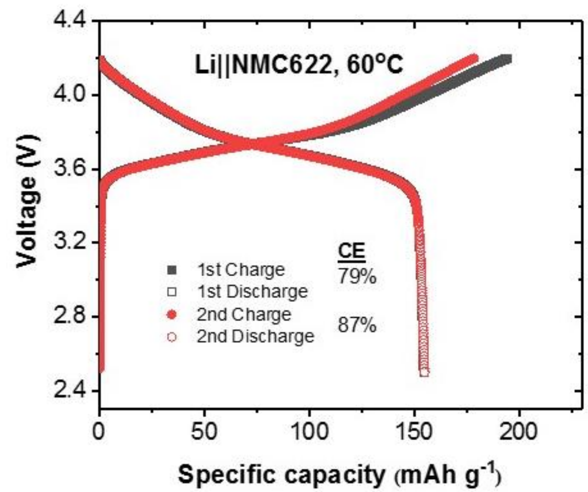

- The polymer-in-salt electrolyte has oxidation stability voltage of 4.5 V on SS substrate.
- Li metal batteries with this polymer electrolyte show reasonable capacities at 60°C.
- More cell testing and polymer electrolyte development are under way.

Responses to Previous Year Reviewers' Comments

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- Comment: One reviewer recommended using thin Li and making sure that the cells are truly Li limited so as to demonstrate the cycle life is not an issue.
- Response: We are currently using thin (50 μm) Li foil to evaluate our electrolytes and will make sure this in future tests.

- Comment: What is additive "X"? The reviewer did not see any value in that.
- Response: The additive "X" on slides 13 and 14 in last year's presentation is $LiAsF_6$. We will make sure to disclose everything to the reviewers in the future.

- Comment: The amount of Li was between 120 and 400 μm, or 24-80 mAh/cm^2. With the cathode at 1.5 mAh/cm^2, this is a massive amount of excess Li and the reviewer questioned the significance of the cycle life.
- Response: We are currently using thin (50 μm) Li foil to evaluate our electrolytes and will also use high loading cathodes (about 3-4 mAh cm^{-2}) to make sure the capacity ratio of negative electrode/positive electrode is in a reasonably small range in future tests.

- Comment: One reviewer said that collaboration is minimal but appropriate at this point in the research.
- Response: We will increase the collaborations with more PIs in other institutions.

Collaboration and Coordination with Other Institutions

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- Argonne National Laboratory: Provided coated NMC cathode sheets for testing.

- U.S. Army Research Laboratory: Provided purified solvents and conducted DSC measurements.

Remaining Challenges and Barriers

- Low Coulombic efficiency of Li metal anode during cycling.
- Cycling stability of Li metal batteries with high loading cathodes.
- Cycling stability of Li metal batteries with limited electrolyte amount.
- Li metal dimension or volume change during charging and discharging cycles.

Proposed Future Work

- Continue the development of hybrid polymer-in-salt composite electrolytes and the evaluation in Li metal batteries.
- Study effects of salt additives on Li metal protection and electrochemical performance of Li metal batteries.
- Increase CE of Li cycling to be ≥99% and achieve 300+ cycles for 4-V Li||NMC cells.

Any proposed future work is subject to change based on funding levels.

Summary

- Investigated effects of Li capacity utilization and charging current density on the stability of Li metal anode.
  - Li capacity utilization changes SEI compositions on Li anode.
  - Slow charge rate leads to a similar Li metal expansion ratio with Li capacity usage.
  - Charge current density has more effect on Li stability than Li capacity utilization.
- Studied effects of four imide-orthoborate dual-salt mixtures on the electrolyte stability and the protection of Li metal anode.
  - LiTFSI-LiBOB shows the highest stability of chemical and electrochemical stabilities.
  - LiTFSI-LiBOB leads the Li||NMC cells to the best cycling stability because of its effective protection on Al substrate and formation of a more robust surface film on Li metal anode.
- Developed new electrolytes based on LiTFSI-LiBOB/carbonate to enhance Li metal battery performances.
  - Optimization of solvent composition and addition of $LiPF_6$ +VC+FEC additive mixture.
  - Optimized electrolyte can significantly stabilize Li metal anode, increase Li CE to over 98%, and improve the fast chargeability and long-term cycling stability of 4.3-V Li metal batteries.
- Investigated the effects of separators on Li metal stability.
  - Different separators would result in different stability with Li metal and thus serious effects on the performances of Li metal batteries, especially in the conventional $LiPF_6$-electrolyte.
  - PE separator is most stable with Li metal.
- Developed high concentration electrolytes and polymer-in-salt electrolytes.
  - High concentration electrolytes have RT conductivity above 1 mS cm^{-1} and good electrochemical stability window.
  - The polymer-in-salt electrolyte has oxidation voltage of 4.5 V vs. Li/Li^+.
  - More development and tests are currently under way.

Acknowledgements

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- Financial support from the DOE Vehicle Technologies Office Advanced Battery Materials Research program is greatly appreciated.

- DOE / BER / EMSL for microscopic and spectroscopic characterizations and computational calculations.

- Team Members:

  Xing Li, Shuhong Jiao, Jianming Zheng, Xiaodi Ren,

  Donghai Mei, Mark H. Engelhard, Linchao Zhang,

  Qiuyan Li, Wengao Zhao, Jinhui Tao, Dehong Hu

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Technical Backup Slides

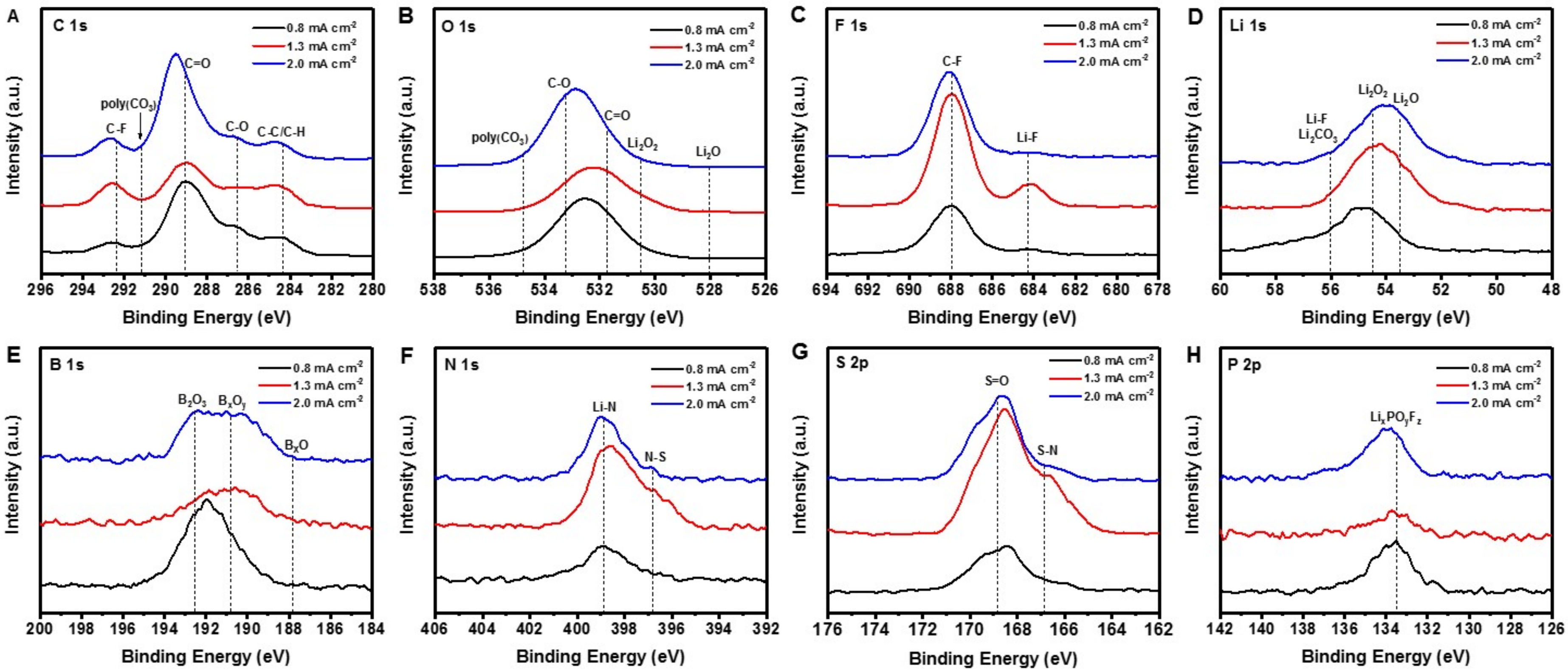
WU XU (PI) and JI-GUANG ZHANG

Pacific Northwest National Laboratory

Project ID #bat275

Technical Accomplishments

XPS of cycled Li metal anodes indicates charge current density affecting SEI compositions



- The major components of the interfaces on the cycled Li metal anodes are similar under different charge current densities, but their compositions in the degradation layers are slightly different.
- **Charge current density affects the compositions of the degradation layer on Li metal anode.**

Technical Accomplishments

XPS of surface films on NMC cathodes in four dual-salt electrolytes indicates different compositions

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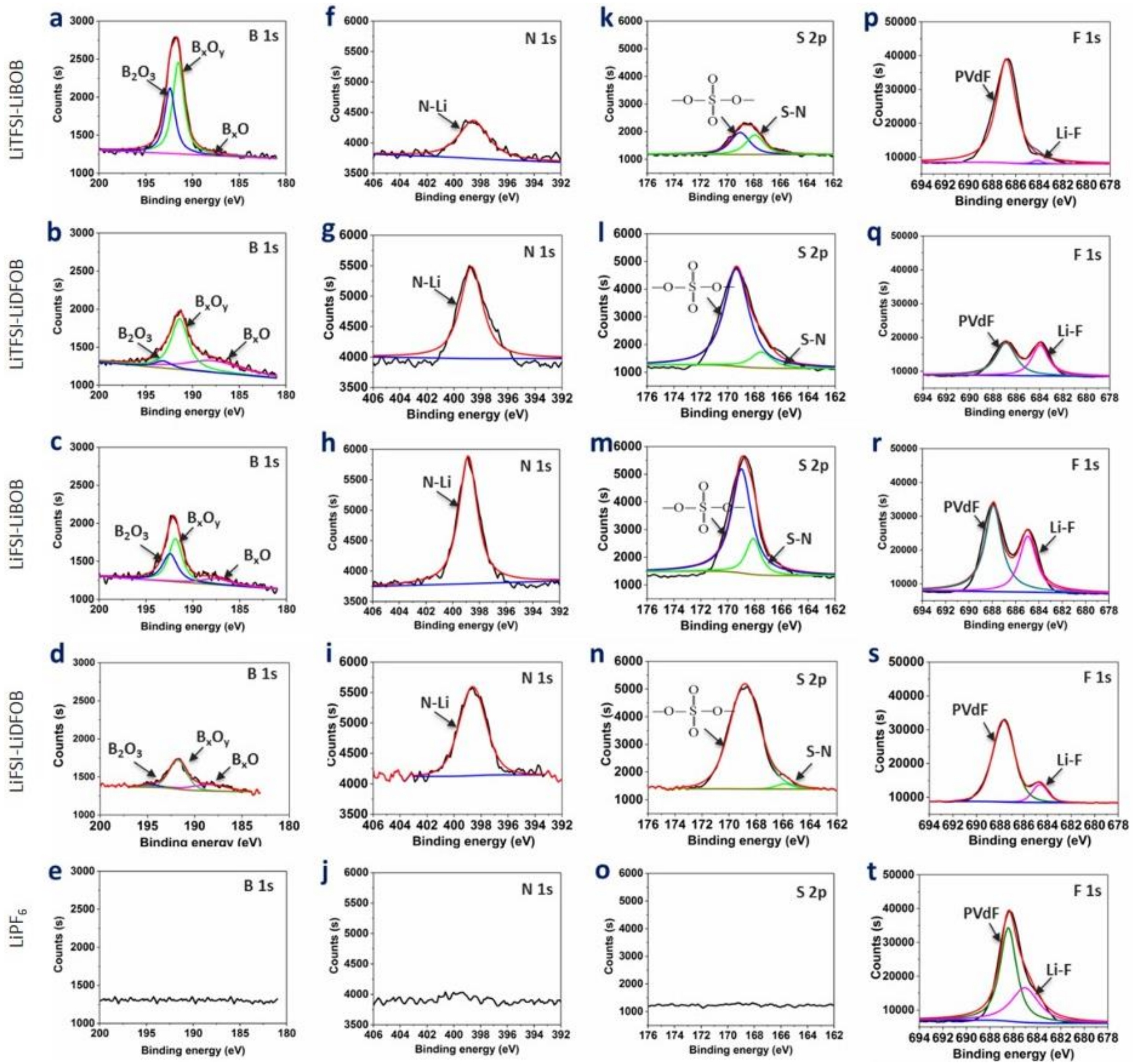

- Different dual-salt electrolytes lead to similar decomposition components on NMC cathode surface, but their compositions are different.
- LiTFSI-LiBOB electrolyte results in the least amount of surface film on the NMC cathode among the four studied dual-salt electrolytes.

Technical Accomplishments

Optimized electrolyte leads to compact and ionic conductive SEI components

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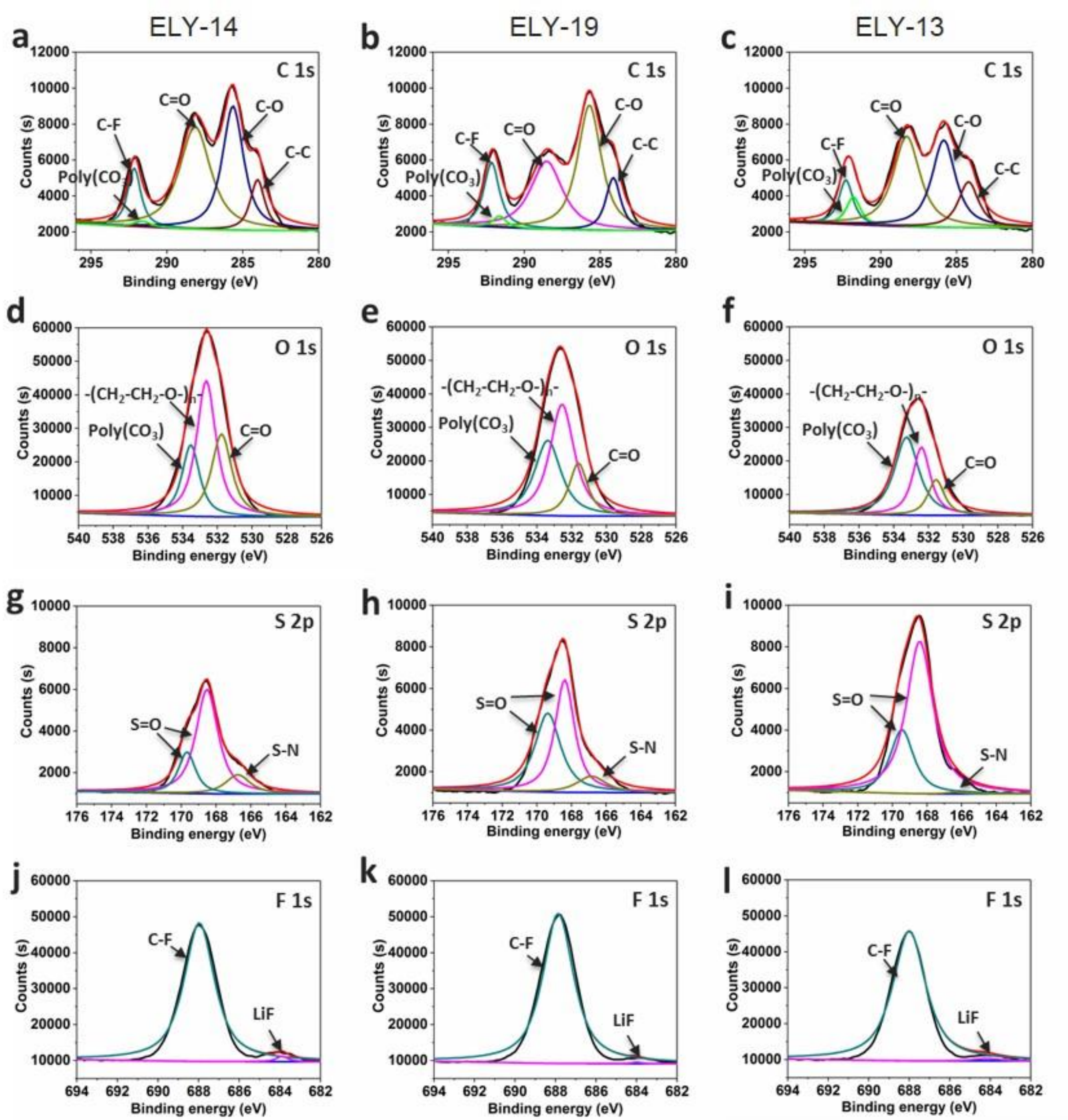
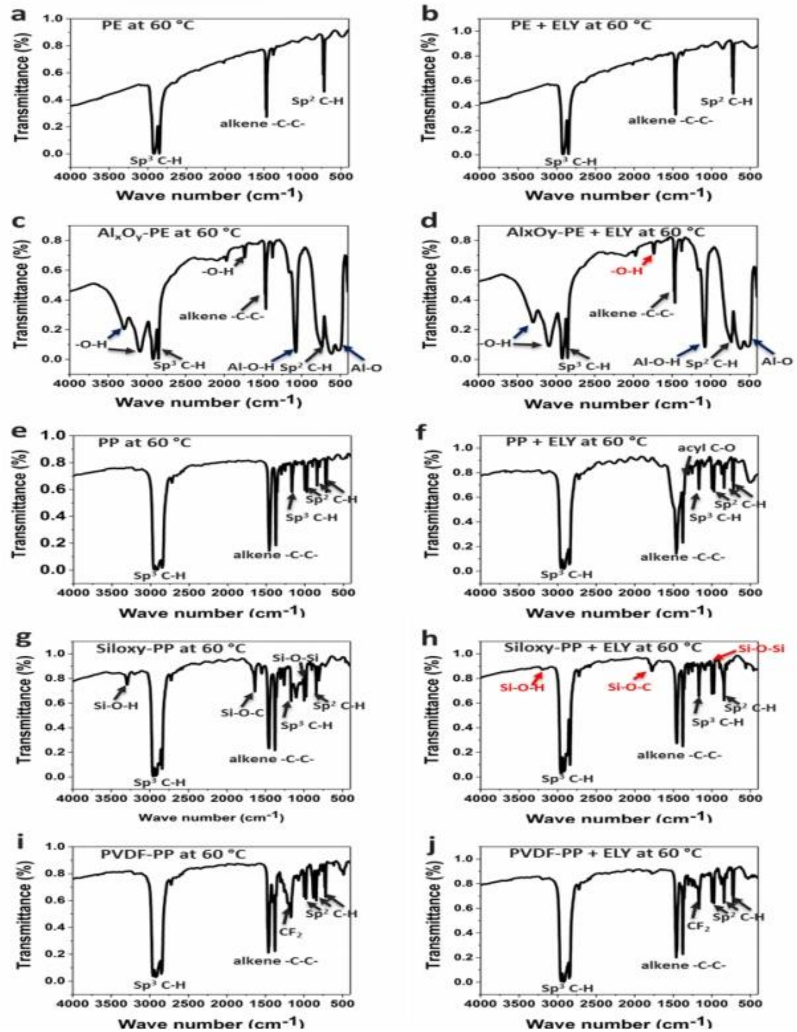
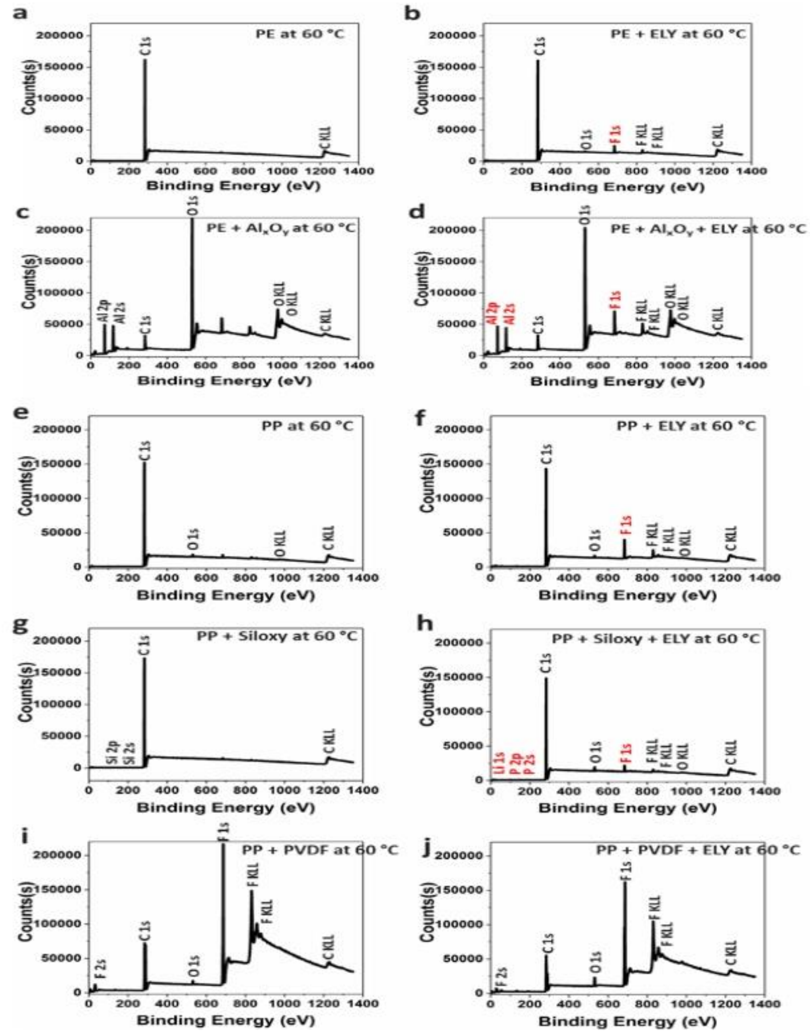


- C 1s and O 1s → The optimal electrolyte ELY-13 with high EC content leads to slightly more ring-opening polymerization of EC to form polycarbonates in SEI on Li → More adhesion to combine inorganic components and to stick to bulk Li.
- S 2p → ELY-13 leads to more S=O species in SEI on Li, which has higher ionic conductivity than LiF and Li_2CO_3.

Technical Accomplishments

FTIR and XPS of cycled separators stored with Li at 60°C/7d w & w/o $LiPF_6$-electrolyte





- Without electrolyte, separators will not react with Li metal.
- With $LiPF_6$-electrolyte, coating layers react with Li but PE and PP will not react.